Studies in Ebullioscopy

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Studies in Ebullioscopy

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STUDIES IN EBULLIOSCOPY

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PART I
THE APPLICATION OF A DIFFERENTIAL THERMOMETER IN EBULLIOSCOPY.

For purposes of molecular weight determination of dissolved substances, the ebullioscopic procedure has certain advantages over the method of cryoscopy. Since, to use the latter, one must for convenience employ solvents whose freezing points lie at easily accessible temperatures, it comes about that water, benzene and acetic acid have been commonly preferred. To obtain satisfactory values for the molecular weight of a solute, it is best to choose a solvent so like it chemically that compound formation shall be at a minimum. To be so closely restricted in the choice of solvents is therefore a disadvantage. Boiling temperatures are, in general, preferable to freezing temperatures as unfavorable to the formation of exothermic compounds. A majority of organic compounds boil normally below 300°. If, as is true, the solvent should differ by at least 150 degrees in boiling point from the solute in order that the volatility of the latter may

not vitiate the results, then, for most practical purposes, the use is indicated of such solvents as boil rather below 100° than above it, and these solvents are in point of fact those most commonly used. The low solubility of certain solutes at the freezing points of the available solvents is a factor against cryoscopy. On the other hand, the precision attainable in cryoscopy has, in the past, been considerably greater than that realized in ebullioscopy, even with apparatus fortified against error by the superimposition of a multiplicity of paraphernalia.

For these and other reasons, a very great deal of work has been carried out by very many investigators with a view to improving the ebullioscopic technique. One may but mention the two dozen papers by Beckmann and his collaborators;[1] and the work of Hite,[2] Orndorff and Cameron,[3] Jones,[4] Ross Innes,[5] Meyer and Desamari,[6] Drucker,[7] Sakurai,[8] Landsberger,[9] Walker and Lumsden,[10] McCoy,[11] Smits,[12] Rijber,[13] Ludlam,[14] Erdmann and Unruh,[15] Lehner,[16] and Turner.[17] Even a single publication by one writer, Hite, reports the trial of over 100 different forms of apparatus. In all these, and many other investigations, the bulb of a mercurial thermometer has been submerged beneath the surface of the boiling solution, and much of the work has been directed to the avoidance of the consequent irregular superheating. In our opinion, the two most successful improvements made since 1892 have originated in this country, the introduction namely, by Bigelow[18] of electric heating, and by Cottrell[19] of a "lift-pump" which pumps the solution over the bulb of the thermometer, which no

[1] References to the numerous papers of Beckmann and his collaborators may be found in the work of Jellinek, "Lehrbuch der Physikalischen Chemie," **2**, 783 *et seq.*, (1915); and also in Staehler's "Handbuch der Arbeitsmethoden in der Anorg. Chemie," **3, i** (1913).

[2] Hite, *Am. Chem. J.*, **17,** 514 (1895).

[3] Orndorff and Cameron, *ibid.*, **17,** 517 (1895).

[4] Jones, "The Freezing-Point, Boiling-Point and Conductivity Methods," Chemical Publishing Co., Easton, Pa., **1912.**

[5] Ross Innes, *J. Chem. Soc.*, **81,** 682 (1902).

[6] Meyer and Desamari, *Ber.*, **42,** 797 (1909).

[7] Drucker, *Z. physik. Chem.*, **74,** 612 (1910).

[8] Sakurai, *J. Chem. Soc.*, **61,** 989 (1892).

[9] Landsberger, *Ber.*, **31,** 461 (1898).

[10] Walker and Lumsden, *J. Chem. Soc.*, **73,** 502 (1898).

[11] McCoy, *Am. Chem. J.*, **23,** 502 (1900).

[12] Smits, *Proc. Acad. Sci. Amsterdam,* **3,** 86 (1900).

[13] Rijber, *Ber.*, **34,** 1060 (1901).

[14] Ludlam, *J. Chem. Soc.*, **81,** 1193 (1902).

[15] Erdmann and Unruh, *Z. anorg. Chem.*, **32,** 413 (1902).

[16] Lehner, *Ber.*, **36,** 1104 (1903).

[17] Turner, *J. Chem. Soc.*, **97,** 1104 (1910).

[18] Bigelow, *Am. Chem. J.*, **22,** 280 (1899).

[19] Cottrell, *J. Am. Chem. Soc.*, **41,** 721 (1919).

longer need be submerged in the solution, but is located above the solution in the vapor phase. When Cottrell's device is employed, there remain outstanding, for non-volatile solutes, the errors inherent in the use of the Beckmann type of thermometer, the error due to uncertainty as to actual concentration of solute, and the very troublesome error due to change of boiling point caused by change of barometric pressure during the observations.[20] This last may, in part at least, be overcome by the employment of somewhat cumbrous "manostats,"[21] by especially constructed aneroid barometers,[22] or by the use of a second, duplicate, apparatus[23] operated simultaneously and containing another Beckmann thermometer immersed in the pure boiling solvent.

In 1910, Menzies[24] had described a simple apparatus, independent of barometric change, which, when properly constructed, gives molecular weights of solutes in solvents at their boiling points by direct measurement of lowering of vapor pressure, without the use of any thermometer. Continuing this effort at simplification, it was found that the differential thermometer described by Menzies,[25] when applied to ebullioscopy with the Beckmann type of apparatus, served only to render more glaring the inevitable irregularities inseparable from that method of procedure. When however, Cottrell's paper appeared in 1919, opportunity was taken to work out the simplest possible apparatus and technique which should free ebullioscopy from all its most serious drawbacks.

The Apparatus.—The diagram, Fig. 1, shows a boiling tube, whose narrowed upper portion itself serves as condenser tube. A glass cylinder, open above and below and of diameter slightly less than the boiling tube, is located concentrically within the latter, and confers the advantages of a double jacket. Within this is supported the differential thermometer, on the lower bulb of which hangs the pump, loosely, as a hat on a peg.[26] The absence of rigid connection diminishes possibility of breakage, besides adding flexibility, literal and metaphorical.[27] The boiling tube is heated

[20] Cf. Meyer and Desamari, *Ber.*, **42**, 2809 (1909), who were misled by this error into obtaining only one-half the true value for the molecular weight of tribromo-resoquinone, and so to assigning to it an inaccurate formula. The practical text-books often recommend postponing ebullioscopy to a day when the barometer is steady.

[21] Cf. Smits, *Z. physik. Chem.*, **39**, 415 (1902); Burt, *J. Chem. Soc.*, **85**, 339 (1904); Drucker, Ref. 7.; Beckmann, *Z. physik. Chem.*, **79**, 565 (1912); etc.

[22] Meyer and Desamari, *Ber.*, **42**, 797 (1909).

[23] Cf. Beckmann, Ref. 1; Washburn and Read, *J. Am. Chem. Soc.*, **41**, 729 (1919); Sluiter, *Proc. Acad. Sci. Amsterdam*, **17**, 1043 (1914).

[24] Menzies, *J. Am. Chem. Soc.*, **32**, 1615 (1910).

[25] Menzies, *ibid.*, **43**, 2309 (1921).

[26] The complete apparatus, with both boiling tube water-and filled thermometer of Pyrex glass, is furnished by Messrs Eimer and Amend, 205 Third Avenue, New York, N. Y.

[27] We have on no occasion yet broken any part of the apparatus.

by direct contact with the low flame of a common Bunsen burner, protected by the customary draughtshield of metal, best in an inverted position. When boiling begins, portions of the liquid in the bulb are carried by the vapor in fragments up the pump and discharged to form a thin film over the lower bulb of the thermometer, which thus attains the temperature at which this liquid, or solution, is in equilibrium with the vapor. The upper bulb acquires the temperature of the pure boiling solvent. The thermometer registers the difference between these two temperatures.

Fig. 1.

Equilibrium is reached so rapidly, except in cases of slow solubility, that fresh additions of solute may be made as fast as they can be weighed out. Contrary to all ebullioscopic tradition, the apparatus will give good results in a room that is not free from draughts. Unlike every other ebullioscopic apparatus, this form is entirely free from all corks, ground glass joints or stoppers.

The sources of error, including that due to barometric change, eliminated by the use of the new type of differential thermometer have been briefly referred to in the preceding article. The advantages gained by removing the lower bulb from immersion in the boiling liquid have been well explained by Cottrell,[19] and confirmed by Washburn and Read[23] and by Spencer,[28] to whose interesting papers the reader is referred for consideration of many matters that cannot be dealt with here. To their remarks may, perhaps, be added that the error due to change of bubble size caused by the marked change of surface tension on addition of certain solutes; that due to change of head of liquid above the thermometer bulb; and the errors caused by fractionation of the solvent and by slow removal by distillation of somewhat volatile solutes, incident to the Sakurai-Landsberger method, are also alike avoided. The chief residual source of error lies in the uncertainty as to the true concentration of the boiling solution as deduced, not by subsequent analysis, but simply from the weights of solvent and solute used. Part of the solvent is absent from the solution in the form of condensate on the walls, and part is absent in the form of vapor. This source of error, ever present in the Beckmann type of apparatus, has often failed of due consideration. To minimize it, we constrict the boiling tube above the lower bulb, mark cc. graduations on the cylindrical neck so developed, and read off the actual working volume of the solvent an instant after ebullition has been caused to cease, while the tube is still wet with condensate and filled with vapor.

[28] Spencer, *J. Am. Chem. Soc.*, **43**, 301 (1921).

A simple water-filled differential thermometer suffices for the range of temperature from the boiling point of water to that of ether, thus embracing the use of such solvents as carbon disulfide, acetone, chloroform, methyl, ethyl and propyl alcohols, methyl acetate and iodide, ethyl formate, acetate, bromide and iodide; carbon tetrachloride, and benzene, and allowing a choice adequate for ordinary purposes. No "setting" of the thermometer is required for the use of different liquids.

Method of Procedure.—The boiling tube is clamped in a vertical position by means of a large single clamp located just under the upper side-tube of the condenser jacket. Beneath it is clamped a Bunsen burner at such a height that when the top of its tube is in position about 1 cm. below the bottom of the boiling tube, the base of the burner is a few centimeters above the sole of the supporting ring-stand. The boiling tube is filled with solvent to the level of the lower graduations of the constricted neck, the condenser water turned on, and the flame lighted and suitably adjusted by means of the customary screw-clip. The boiling point of the solvent is now taken to the nearest tenth of a degree by means of a good ordinary thermometer, in which operation the avoidance of exposed thread is usually easy. While the thermometer used for this purpose is reaching thermal equilibrium, the barometer may conveniently be read, and information thus obtained as to the purity of the solvent. The actual working volume of the solvent is next found by lowering the burner (not its gas supply) so that it is ready to be swung clear, quickly swinging it aside, and causing instant cessation of bubble formation by immersing the bottom of the boiling tube in cold water raised by hand from below in a small beaker. The reading of volume—best against a white card in the background—should be made immediately ebullition is caused to cease, before the access of solvent that drains from the walls. The burner is then replaced in position. For purposes of molecular-weight determination, one may employ as ebullioscopic constant the boiling-point rise in degrees produced by one mole of solute per 100 cc. of solvent at its boiling point (K_2 in Table I p. 2320). The mercurial thermometer is now withdrawn, the pump introduced and lowered to the bottom of the boiling tube by means of a deep hook on the end of a wire, and the differential thermometer inserted, engaged on the pump, and clamped in suitable position by the end of its handle which is made wide so as to be more easily gripped by the clamp. While temperature equilibrium is being reached, which may occupy 15 minutes, it is convenient to prepare pastilles of the solute and to make the first weighing of the bottle containing them.

In making readings of the differential thermometer, the error of parallax may be simply avoided by fixing a white card, of the size of a postal card, with bold graduations in centimeters across it corresponding to those on the thermometer, at a suitable distance behind the latter at the same level,

and placing the eye so that the readings on card and thermometer correspond. The zero reading is given by the difference between the readings on the stem and on the lower bulb, and its value obviously serves as a most useful index of the purity of the solvent. Unsteadiness of reading is caused by too slow boiling.

A pastille of solute is now dropped, from forceps, down the condenser. If it be easy of solution, the reading will at once rise and become constant the moment solution is complete. The ebullioscopic rise is obtained by subtraction of the zero reading from the difference of level now observed. This is later translated into temperature at leisure by the help of a conversion factor extracted from such a table as that given in another communication.[25] It is to be noted that, for fine work, in order to obtain the true conversion factor, one must use as argument the average temperature of the two ends of the thermometer, which is higher than the boiling point previously found by the mercurial thermometer by an increment of temperature corresponding to half the observed ebullioscopic rise. If half the ebullioscopic rise multiplied by the factor selected by a first inspection does not, when added to the boiling point of the solvent, yield a temperature that agrees with the chosen factor, then the factor may be reselected accordingly.

Case of Volatile Solutes.—It is generally agreed[29] that, for purposes of straightforward molecular weight determination, the boiling point of an ebullioscopic solvent should lie at least 150° below that of the solute. For this reason, benzil (b. p. 347°) has found favor as a standardizing solute because it may be assumed to be virtually absent from the vapors escaping from its solution in the common ebullioscopic solvents. If, however, the solute be as volatile as naphthalene (b. p. 218°) in boiling carbon tetrachloride or benzene, then one would anticipate that the mixed vapors, on partial condensation, would tend to yield a liquid of the concentration with which they are in equilibrium, namely the concentration of the solution from which they have just escaped. The upper bulb of the differential thermometer might thus be expected to acquire precisely the same temperature as the lower bulb; and, if precaution be taken to minimize condensation on the thermometer, this condition can indeed be approximated. The gross composition of the vapor phase, however, is close to that of the pure solvent, so that if this vapor is completely condensed and caused to lave the upper portion of the differential thermometer, the temperature it acquires in contact with the surrounding vapor is very close to the boiling point of the pure solvent, which is the temperature here desired. In order to provide an adequate laving of this kind, a very simple plan is to embrace the handle of the thermometer, at a point a few centimeters above the upper bulb, with a pair of wires of

[29] Cf. Staehler, Ref. 1.

perhaps 24 S. W. G. twisted together where they meet on opposite sides of the handle, and to direct the two twisted tags so formed upwards in such a way that, by resting against the inner walls of the condenser tube, they may uniformly divert a modicum of the condensate on to themselves and thence to the thermometer. The diagram, Fig. 2, shows these wires, which are prevented from slipping either up or down by reason of the slight constriction in the handle where they are applied. In practice it is useful to employ these wires in all cases, not only because of possible prejudicial volatility of the solute, but to meet the contingency of spattering of the upper portion of the thermometer by minute droplets from a frothing solution. The wires may also very conveniently be bent so that the handle of the thermometer is stationed sufficiently eccentrically within the condenser tube as to allow a very clear passage for the introduction of pastilles. This is indicated in Fig. 2 (b).

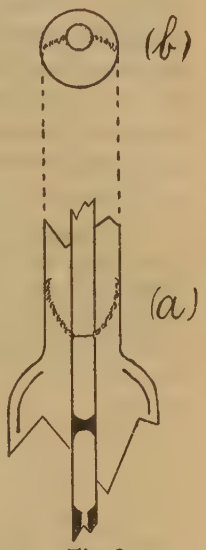

Fig. 2.

Collected Useful Data.—In Table I are collected, from diverse sources, certain useful data for a few of the commoner solvents: their normal boiling points; the barometric change, dp/dt, in mm. of mercury that produces a change of 1° in the boiling point; the density, D, of the liquid at the boiling point; its change, dD/dt, per degree of temperature; the ebullioscopic constant, K_1, for one mole of solute in 100 g. of solvent; the ebullioscopic constant, K_2, for one mole of solute in 100 cc. of solvent at its boiling point.

TABLE I.

CONSTANTS USEFUL IN EBULLIOSCOPY.

Solvent.	B. p. °C.	dp/dt	D.	dD/dt.	K_1.	K_2.
Acetone	57.0	26.4	0.7922	0.0011	17.2	22.9
Benzene	80.1	23.4	0.8149	0.0010	26.1	32.0
Carbon disulfide	46.3	24.7	1.2223	0.0016	23.7	19.4
Carbon tetrachloride	76.8	23.3	1.4801	0.0021	48.0	32.4
Chloroform	61.2	25.2	1.4101	0.0018	39.0	27.7
Ethyl acetate	77.2	25.1	0.8302	0.0010	27.9	33.6
Ethyl alcohol	78.4	30.3	0.7889	0.0011	11.7	15.8
Ethyl ether	34.6	26.9	0.6968	0.0011	21.6	31.1
Methyl acetate	57.1	26.8	0.8802	0.0014	20.6	23.4
Methyl alcohol	64.7	29.6	0.7468	0.0010	8.8	11.8

The values for K_1 are taken chiefly from Staehler's *Handbuch*[1] as an impartial source. We doubt the accuracy of some of these values. It must be remembered that the values determined and adopted by even a single investigator such as Beckmann, for example, have varied from time to time. The matter will be reverted to on another occasion. The change

of the ebullioscopic constants with barometric pressure is of the order of 0.3% per 10 mm. near 760 mm.

Examples of Results.—We shall here limit ourselves to a very few typical cases to illustrate merely the consistency of the results obtainable by the use of this apparatus, and their general agreement with the results of others. For a later redetermination of certain ebullioscopic constants, especial purification of materials and other precautions will be required; but for the present purpose the ordinary materials of the laboratory supply-room have proved sufficient. In order to conform to the practice of Beckmann and most others, we have employed in computing our results the well-known simple, if inadequate, relationship K_1 = temp. rise × mol. wt. of solute × wt. of solvent ÷ 100 × wt. of solute.

(a). **Benzil in Benzene.**—Values of the ebullioscopic constant K_1 used by Beckmann[30] were 26.7 (1890), 26.1 (1895), 24.2 (1905), 25.7 (1907, 1914). Drucker[7] found 26.7, Innes[5] 24.1, etc. Beckmann's present accepted value, 25.7, is the mean of two sets of each three measurements with benzil in benzene, as follows: (1) rise, 0.180°, 0.354°, 0.568°, corresponding respectively to K_1 = 25.7, 25.6, 25.2: (2) rise, 0.205°, 0.450°, 0.688°, yielding K_1 = 25.6, 26.2, 25.7. We made two sets of

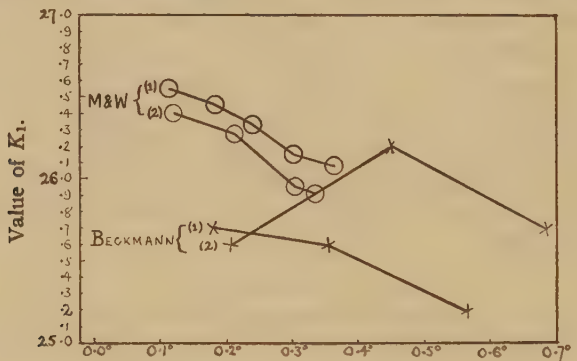

Fig. 3.

measurements, on different days, as follows: (1) rise, 0.1142°, 0.1820°, 0.2440°, 0.3016°, 0.3661°, corresponding respectively to K_1 = 26.6, 26.5, 26.3, 26.2, 26.1: (2) rise, 0.1218°, 0.2126°, 0.3052°, 0.3355°, yielding K_1 = 26.4, 26.3, 26.0, 25.9. The fourth significant figure has some meaning for our higher readings. From these data, which are shown plotted in Fig. 3, it would appear that the values in each of our sets are rather more self-consistent than those of Beckmann, although obtained with much simpler apparatus; and that 0.1 mm. on the scale of the differential thermometer may be estimated successfully. Our two sets differ from each other, on the average by 0.6%, an error that would be caused by an error of 0.2 cc. in reading 30.0 cc., the approximate volume of benzene employed. As we have learned from many other results, this is the largest value to which this error ever attains; more often the error from this cause is 0.1 or 0.0 cc., averaging well under 0.5% in the result. Aside from possible systematic error, it is the chief single source of error entering into our determi-

[30] Cf. Beckmann, *Z. physik. Chem.*, **88**, 23 (1914); **58**, 555 (1907).

nations. The details of the observations of Set 1 follow, serving to illustrate the use of conversion factor and to indicate the time consumed.

TABLE II.

OBSERVATIONS OF SET 1.

Volume of benzene at the boiling point, 31.6 cc. Boiling temperature, corrected, 79.7°. Barometric reading, corrected, 755.2 mm. Solute, benzil, 210.1.

Obs. No.	Time. h. m.	Wt. of benzil. G.	Diff. therm. reading. Mm.	Conversion factor.	Rise. °C.	K_1.
0	1.26	0.0	10.5 (zero)	.....	0.0	...
1	1.32	0.2326	22.8 (above zero)	0.005011	0.1142	26.56
2	1.36	0.3726	36.4 (above zero)	0.005005	0.1820	26.46
3	1.41	0.5011	48.8 (above zero)	0.004999	0.2440	26.33
4	1.46	0.6238	60.4 (above zero)	0.004994	0.3016	26.16
5	1.52	0.7595	73.4 (above zero)	0.004988	0.3661	26.08

(b). Anthracene in Chloroform.—Benzol, alcohol and chloroform are perhaps the three best-studied ebullioscopic solvents, and we chose this example because, in particular, the Sakurai-Landsberger method has been critically studied by Turner[17] who used it to redetermine the constant for chloroform. Of Turner's solutes, anthracene was most readily available to use in reasonably pure form.[31] Because of its ease of decomposition, we do not regard chloroform as so suitable an ebullioscopic solvent as carbon tetrachloride, which covers a similar field of solutes.

In the two sets of experiments for which he gives data, Turner obtained the following results: (1) rise, 0.646°, 0.527°, 0.436°, 0.363°, corresponding respectively to K_1 = 40.5, 40.4, 40.5, 40.3; (2) rise, 0.559°, 0.455°, 0.376°, yielding K_1 = 38.3, 38.0, 38.5. In two sets of experiments we obtained, (1) rise, 0.2672°, 0.3981°, 0.5045°, 0.6213°, yielding K_1 = 39.58, 39.42, 39.09, 38.66; (2) rise, 0.3166°, 0.4042°, 0.4792°, 0.5565°, 0.6515°, yielding K_1 = 39.90, 39.25, 38.56, 38.59, 38.09. Turner averages his two sets at 40.4 and 38.3 respectively—results discrepant by 5.4%, or 2.7% from their mean. Our results, when plotted, diverge from a straight line drawn through them by 0.56% on the average. It may be said that the impure chloroform used does not show our method to advantage. The unsatisfactory character of chloroform as an ebullioscopic solvent is further indicated by the rather wide variation of the values for the constant employed by Beckmann from time to time, ranging from 35.9 (1895) to 39.0 (1908).

(c). Naphthalene in Ether and in Carbon Tetrachloride.—It is necessary to add these further examples to illustrate the use of an appreciably volatile solute. In a single run in which we added 8 successive quantities of naphthalene to ether of normal boiling point, 34.1°, with consequent elevations of temperature ranging from 0.27° to 2.04°, we obtained values for K_1 of 21.47, 21.43, 21.11, 20.68, 20.39, 20.31, 19.82, 19.77, results which diverge on the average by about 0.33% from a straight line drawn through their plot. If, however, the twisted wires described above were omitted in this case, the results obtained were low and unsatisfactory. It should, perhaps, be added that one does not expect strict rectilinearity in the graph obtained as above; and that, in the case of ether, which has a considerable vapor pressure at the temperature of the condenser, a small correction, under 1% per hour, might be made for progressive loss of solvent by diffusion into the air. A straight line, however, is undeniably a smooth curve, for purposes of reference.

Carbon tetrachloride boils only 141° below naphthalene, thus falling within the forbidden range of 150° referred to above. To secure more copious laving of the upper

[31] Through the courtesy of the Chemical Department of the Barrett Co.

portion of the thermometer by the condensate in this case, we employed twisted double wires instead of single wires in constructing the drainage mechanism, and opened the ends in contact with the condenser tube so as to form forks, thus withdrawing the condensate from the walls at four points each served by a pair of wires twisted together. This had the effect of raising the zero reading by a few millimeters. Using a solvent of normal boiling point, 76.2°, we obtained, from elevations of 0.1888°, 0.2822° and 0.3990°, values for K_1 of 47.23, 47.89, and 48.46. For computation merely the simple relationship mentioned above was utilized, without correction for volatility of the naphthalene. Benzene as solvent for naphthalene gave results of similar quality, thus demonstrating that usable results may still be obtained even in these somewhat adverse cases.

Summary.

A simple apparatus for ebullioscopy has been described and illustrated in which is employed a new type of differential thermometer. Most of the sources of experimental error that have influenced the very many earlier forms of ebullioscopic apparatus have here been avoided or so minimized that results consistent to within 0.5% are readily obtained.

PART II

THE INFLUENCE OF THE PERIOD OF HEATING UPON THE BOILING POINT OF CERTAIN LIQUIDS USED IN EBULLIOSCOPY, WITH A NOTE ON TESTING THE PURITY OF VOLATILE LIQUIDS BY ISOTHERMAL DISTILLATION.

This part describes a series of experiments designed to determine as accurately as possible whether the boiling point of a liquid is dependent upon the liquid's previous thermal history, *i. e.*, whether a liquid which has been boiling for several hours, boils at exactly the same temperature as one recently elevated from a lower temperature. It is obvious, as pointed out by Smits and others, that in associated liquids there might be a delay in attaining the degree of association appropriate to the higher temperature. This would usually result in a slightly higher boiling point at the beginning of ebullition than would be observed several hours later. For purposes of investigation two associated liquids, bromine and acetic acid, and two supposedly non-associated liquids, benzene and carbon tetrachloride, were used.

We also briefly refer to a method of testing the purity of volatile liquids, far more sensitive than the ordinary methods of boiling point and distillation range.

This study was prompted by experiments reported by H. B. Baker,[2] who believed that they demonstrate a delay in the attainment of internal equilibrium in the case of bromine and acetic acid. These observations, if confirmed, might serve to explain several difficulties previously encountered in ebullioscopic work, such as (1) the frequently mentioned necessity of allowing an astonishingly long period of time for the pure solvent to attain a constant boiling point in Beckmann's ebullioscopic method of determining molecular weights,[3] (2) the classical controversy[4]

[2] Baker, *J. Chem. Soc.*, **129**, 949 (1927).

[3] Beckmann, *Z. physik. Chem.*, **6**, 473 (1890); **8**, 225 (1891). Biltz, translated by Jones and King, "Practical Methods for Determining Molecular Weights," **1912**, p. 155; Jones, "The Elements of Physical Chemistry," 4th ed., **1915**, p. 133; Walker, "Introduction to Physical Chemistry," 9th ed., **1922**, p. 200; Findlay, "Practical Physical Chemistry," 4th ed., **1923**, p. 264.

[4] Reference to the extensive literature on this subject may be found in Ostwald's "Lehrbuch der Allgemeinen Chemie," Vol. I, p. 308.

as to the equivalence of the static and dynamic methods of vapor pressure determination, (3) the frequency with which it is found that the most satisfactory vapor pressure curve of a liquid shows a temperature at 760 mm. pressure not identical with the best observed boiling point determinations. Raikes and Bowen[5] pertinently remark that this discloses a "situation which can be cleared up only by further research."

Experimental Method

The method in brief consisted of a differential reading between two isoteniscopes,[6] one containing a portion of the liquid which had been held near the boiling point for several hours, the other containing a portion recently rapidly elevated to the same temperature by insertion in the bath. Isoteniscopes, being compact in form, can be used in a bath designed for more adequate stirring than can be supplied for long barometer tubes. This, with the fact that the liquid under consideration is used as a manometric fluid instead of the denser mercury, and that the readings are differential and not absolute in nature, allows a far greater sensitivity[7] than that attained by Baker. The observations were continued until the liquids were more similar in thermal history. A difference in vapor pressure observed at first and not disappearing within a reasonable time must be due not to difference in thermal history but to some of the other factors discussed later.

Apparatus.—The isoteniscopes were constructed of pyrex glass, the bulb of 35-cc. capacity, being sealed to thick-walled tubing of 2 mm. bore which formed the left side of the manometer. The right side was of 10-mm. tubing in which, above the level of the bath, were blown four elongated bulbs to serve as the inner tube of a condenser 27 cm. long. Near the end it was bent at a slightly acute angle to prevent possible contamination from the rubber connections. Each isoteniscope was connected through a short piece of rubber tubing to a tube containing calcium chloride, thence through a long flexible tubing to a 1-liter flask which served as a reservoir to stabilize the pressure and facilitate delicate adjustment. Mercury manometers connected with these flasks were a convenience in manipulation. By means of glass and rubber tubing fitted with suitable clamps, it was possible to establish pressure equality between them, and to adjust both or either of them to any desired pressure not greater than atmospheric. The arrangement is shown diagrammatically in Fig. 1.

The bath consisted of a 3-liter beaker filled with glycerin and stirred by a six-bladed glass stirrer electrically propelled. Adjacent were two heating units and the expansion bulb of the thermostat. Near the front of the bath was a bakelite millimeter scale supported vertically. The scale was 120 mm. long and the markings were about 5 cm. wide, so that when the isoteniscopes were in position, the bulbs hung over the top of the scale near the center of the bath, while the manometers, side by side in front of the scale, could be read almost simultaneously. Except for windows at the front and back,

[5] Raikes and Bowen, "International Critical Tables," Vol. III, 1928, p. 215.

[6] Smith and Menzies, *J. Am. Chem. Soc.*, **32**, 1412 (1910).

[7] The sensitivity is illustrated in the last column of Table I, which shows the temperature change corresponding to a pressure change of 1 mm.

the beaker was insulated with cotton wool. A lamp behind the bath furnished illumination. The heating units and the thermostatic control were so connected with rheostats that the difference between the current intensities during the "on" and the "off" periods could be reduced to a minimum at the time of reading, thus diminishing the "pumping" effect referred to later.

Procedure.—Except in the case of bromine (*q. v.*) the liquid was taken up in a dried pipet and 5 cc. placed in each of the thoroughly cleaned and dried isoteniscopes, which were immediately connected to the vacuum system. The permanent gases were removed as far as possible by repeatedly boiling out near room temperature. With water running through the condensers, the isoteniscope was evacuated to a pressure corresponding to the vapor pressure a few degrees above room temperature. A small flame was then applied intermittently to the bottom of the bulb. The vapor passed through the manometric portion of the isoteniscope carrying the dissolved gases with it and, condensing, formed a trap which prevented their readmission. By allowing the bulb to cool, the greater part of the liquid was returned to it, leaving sufficient in the manometer to form a trap. When this had been repeated several times with each isoteniscope, comparison in the bath at room temperature showed that their vapor pressures agreed within the experimental error and further boiling out caused no change. After the final comparison, isoteniscope A was removed from the bath and by closing clamp 1 was cut off from the rest of the system. The heat was then turned on and the pressure over the liquid in B allowed to increase as the vapor pressure rose. When the pressure had increased to within a few centimeters of 76, the thermostat was set to hold the bath at the corresponding temperature. The isoteniscopes were allowed to stand thus, A at room temperature, B near the boiling point, for about four hours. The position of the manometric liquid was watched during that time and any necessary adjustments made to prevent the entrance of air into the bulbs. Near the end of this period the pressure on B was reduced slightly so that bubbles of vapor passed through the confining liquid and condensed, thus eventually evaporating all the liquid from the bulb. Meanwhile, by slightly warming A, the liquid in that isoteniscope also was condensed in the wide arm of the manometer. At this point clamp 2 was closed, the connecting tubes evacuated and clamp 1 opened, allowing the pressure on A to be altered without affecting B. Isoteniscope A was then placed in the hot bath and by means of clamp 3 the pressure was increased as rapidly as possible without forcing any liquid into the bulb. When the behavior of the liquid in A indicated that temperature equilibrium was near attainment, clamp 2 was opened, thus assuring the identity of the external pressure on the two isoteniscopes. As rapidly as possible the greater part of the liquid in both isoteniscopes was returned to the bulbs and comparative vapor pressure readings taken. Agitation of the liquid in the bulbs hastened temperature equilibrium. When A was inserted without the precautions noted above, the sudden inflow of heat from the large surface of the

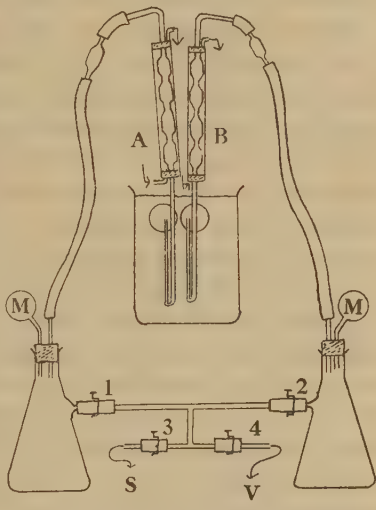

Fig. 1.—Diagram showing apparatus with isoteniscopes in position for reading. A, B, isoteniscopes; 1, 2, 3, 4, clamps; M, mercury manometers used for convenience in adjustment. S, to air; V, to vacuum.

bulb caused instant and complete evaporation, with considerable loss of liquid. This procedure, by reducing the heating surface, allowed the increase of pressure to keep pace with the speed of heating.

The constant "pumping" movement of the manometric liquid due to small fluctuations of bath temperature was reduced as much as possible by proper rheostat adjustment. To minimize the error from this source the reading was made as far as possible at the time of momentary rest between rise and fall of temperature, the pressure being so adjusted that at that instant the menisci in A were level. The pressure difference was then read on the manometer of B. When the liquid in the wide arm of B was higher than in the capillary, it indicated that the vapor pressure of A was less than that of B. Such readings were recorded as negative. Readings were made at frequent intervals until they became constant, and then occasionally for a longer period.

Isothermal Distillation.—When the readings were completed, it was found advisable to test the purity of the liquids by isothermal distillation. The deficiency of this method as a means of measuring or even detecting impurities has recently been discussed by Washburn.[8] The data forming the basis of his discussion are, however, limited to the difference between the vapor pressure of the liquid with an infinitely large and an infinitely small vapor phase. The method here described, in that it furnishes a few intermediate points, is more promising and was found useful in testing at least the *relative* purity of the two samples.

The fractionation was generally carried out immediately after the completion of the main experiment, when both samples of liquid were already at the boiling point and supposedly free of permanent gas. By closing clamp 1, and reducing the pressure, bubbles of vapor could be made to pass through the manometer of B and, condensing, increase the volume of the manometric fluid. The speed of this evaporation could be controlled by the amount of change of pressure. By continuous agitation of the liquid in the bulb, and slow rate of evaporation, the condition is approached where the condensing vapor is of the composition in equilibrium with the liquid. At any point the distillation could be interrupted, temperature equilibrium reëstablished and the change of vapor pressure in B observed by comparison with A. At the same time, the volume of the liquid in the manometer (previously calibrated against the millimeter scale) was read. Thus, by a series of observations, there could be plotted against the percentage of the original amount of liquid in the bulb, the corresponding reduction in vapor pressure. The points obtained are shown in Fig. 2, in which the lowering is expressed as percentage of saturation vapor pressure which in all cases was close to 760 mm. The points for a sample of acetic acid less pure than that used are included for comparison, as is also a line showing the points to be expected by a liquid containing one mole of a non-volatile solute in 9999 moles of solvent. Where the impurity is volatile, the theoretical curve will vary with each pair of substances according to the behavior of their partial vapor pressures. It may be seen

[8] Washburn, *Z. physik. Chem.* (Cohen Festband), 592 (1927).

at a glance, however, that the benzene and bromine used in these experiments are of a higher order of purity than the acetic acid.

The most striking feature of this method of isothermal distillation is its sensitivity. Constancy of boiling point, a generally accepted criterion of purity, is crude in comparison, for the acetic acid used, which distilled completely within a range of 0.02°, was found, on isothermal distillation, to show vapor pressure changes up to 58 mm. of acetic acid (used as manometric liquid) in the course of the fractionation.[9] This acid had been subjected to fractional crystallization twelve times, until the melting point became constant within 0.02°, and was then distilled twice, all but a

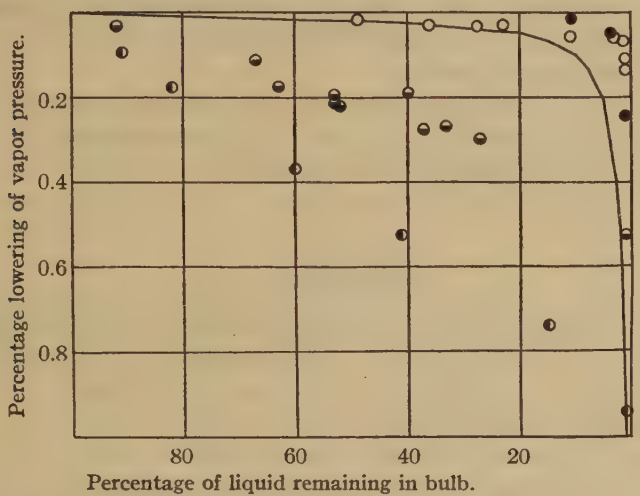

Fig. 2.—Graph showing the fall in vapor pressure resulting in progressive evaporation of liquid by slow isothermal distillation. Fall in vapor pressure is expressed as per cent. of saturation pressure (near 76 cm.). The line represents the theoretical curve for a non-volatile solute. ○, Benzene; ●, bromine; ◒, acetic acid, m. p. 16.6°; ◐, acetic acid, m. p. 16.4°.

negligible residue coming over within a range of 0.02°, m. p. 16.6°, b. p. 117.8°.[10] These figures are in agreement with the best observations in the literature. In this case, therefore, fractionation as here carried out furnished the only evidence of the impurity undoubtedly present.[11] Im-

[9] Fifty-eight mm. acetic acid; density 0.94 ≡ 4.0-mm. mercury, density 13.6 ≡ 0.53% of 760 (Fig. 2).

[10] The thermometers used for testing the purity of liquids were compared with a standard thermometer, whose certified accuracy was 0.1°. The constancy of the readings could be estimated more closely as the thermometers were graduated in 0.2°. Unless otherwise stated, boiling point observations are corrected to 760 mm. pressure.

[11] Lack of this evidence was undoubtedly the cause of the difficulties encountered by Meyer and Jaeger, *Ber.*, **36**, 1555 (1903), and Kahlbaum, *ibid.*, **16**, 2479 (1883), in working with acetic acid.

purities, therefore, too small in amount to be detected by ordinary means are capable of causing appreciable error in vapor pressure measurements where the circumstances are favorable to fractionation.

Errors.—Fractionation as a source of error in our results is eliminated by the expedient of evaporating all the liquid from the bulbs of both isoteniscopes immediately before the comparison is made. The liquid on condensing is thoroughly and automatically mixed by bubbles of vapor passing upward through it. On returning the liquid to the bulbs, one is then certain that the vapor pressures observed are those of the whole mixed portions of liquid. Error from parallax was negligible, because it was suffered alike by each limb of the confining liquid within the isoteniscopes; this was tested also by the very close agreement of two isoteniscopes in the bath under like conditions.

The most important single source of error remaining was the constant movement of the manometric liquid in the isoteniscopes. In Table I, Col. 5, is shown the amount of movement that would be caused by a variation of 1° in the bath temperature.

TABLE I

COLLECTED USEFUL DATA

Liquid	Temp. expt., °C.	Density at the b. p., g. per cc.	Factor, mm. liquid to mm. Hg	At normal boiling point p in mm. liquid dp/dt, mm. liq.	At normal boiling point dt/dp liq., °C.
Acetic acid	117.5	0.94	0.069	346	0.0029
Bromine	58.8	2.98	.219	115	.0087
Carbon tetrachloride	75.0	1.48	.109	213	.0047
Benzene	79.4	0.81	.060	392	.0026

Actually, by adjustment of the rheostat and making the reading in the manner described, the error of reading the pressure difference at the boiling points was probably not greater than ±1 mm. At room temperature these fluctuations were entirely absent. Temperature variation was significant only on account of this "pumping" effect. The actual temperature of the bath was of importance secondary to that of its constancy of temperature. Traces of impurity, if present in both samples in the same amount, produce no appreciable effect on the differential vapor pressure readings. Minute differences in the amount of impurity in the samples contained in the two isoteniscopes, however, produce considerable effect. Except in the case of bromine there was a possibility of absorption of moisture in transferring the liquids to the isoteniscopes. A greater source of error was the possible presence of permanent gases, even after boiling out and comparing the isoteniscopes at room temperature. Any traces of gas dissolved in the liquid or adsorbed on the inner walls of the isoteniscopes would tend to enter the vapor phase during the heating. Any such accumulation in B would be removed when it was boiled out just before the insertion of A, but in A the heating was of necessity deferred until the readings were to be

made and the accumulating gas would cause a gradual increase in the apparent vapor pressure of A as compared to B. This was an error of the second order in all experiments but benzene (a), which was continued for ten hours. In this case a gradual increase of pressure amounting to 0.1 mm. of mercury was noted. Though nearly within the experimental error from other sources, it appeared to be quite definite, and could be accounted for by the liberation of only 0.004 cc. of permanent gas.

TABLE II

EXPERIMENTAL DETAILS FOR ACETIC ACID

Temp., 117.5°; period of heating B, 4 hrs., 50 min.

Time elapsed since insertion of A		Vapor pressure diff. obs.		Diff. in b. p. indicated, °C.
Hrs.	Min.	Mm. liq.	Mm. Hg	
	9	−6	−0.41	+0.017
	12	−4	− .28	+ .012
	8	−2.5	− .17	+ .007
	21	−2.5	− .17	+ .007
	33	−2.5	− .17	+ .007
2	42	−2.0	− .14	+ .006
4	10	−2.5	− .17	+ .007

Results

Detailed experimental data are reported in only one instance for purpose of illustration. The results for all liquids are summarized in Table III. Information not readily tabulated is given under the heading of each liquid. The observations of pressure difference are given to the nearest 0.5 mm., as in some cases, notably those of bromine and carbon tetrachloride, this refinement of measurement has probably some significance, due to a diminished amount of pumping. The time required to heat the bath to the boiling point of the liquid varied from fifteen minutes in the case of bromine to eighty minutes in the case of acetic acid. The period of heating was not considered to have started until the boiling point was attained.

Acetic Acid.—The purity of this material has been discussed. Experimental details are shown in Table II. The pressure difference observed indicated that the more recently heated portion possessed a vapor pressure 0.17 mm. of mercury lower than that heated for about five hours. This is in the direction suggested by Baker's results, but there was no change in this difference over a period of four hours, at which time the thermal history of the two samples was more nearly similar.

Bromine.—This was prepared from recrystallized potassium bromide and purified by the method of Robinson and Briscoe.[12] It was then dried in contact with fused calcium bromide prepared from a portion of the pure bromine. The isoteniscopes were in this case sealed to the drying tube,

[12] Robinson and Briscoe, *J. Chem. Soc.*, **127**, 142 (1925).

after which the system was evacuated and allowed to stand for a week. Finally 5 cc. of bromine was distilled into each isoteniscope, which was then sealed off, the tip being later broken after connection to the vacuum system. The desirability of this method of treatment is reflected in the results. The bromine used had not been elevated above room temperature for three months previous to the experiment; vapor pressure 760.5 mm. at 58.8°. Isothermal distillation indicated a very high order of purity. There was no difference observed between the pressures of the two samples and no change in this condition over a period of four hours.

Carbon Tetrachloride.—The original liquid boiled at 76.6° within a range of 0.05°. The middle portion was retained and kept for eighteen months in contact with metallic calcium. This was an early experiment, completed before the disturbing effect of fractionation had been observed. In this case, instead of evaporating all the liquid from both bulbs immediately before making the comparison, B was not allowed to boil out, while A of necessity boiled out completely on immersion. No test of purity by isothermal distillation was made.

Benzene.—A high quality commercial product was shaken successively with sulfuric acid, sodium hydroxide and water, and dried over fused calcium chloride. On distillation it boiled at 80.1°. It then stood for twenty-two months at room temperature, for twenty months in contact with metallic calcium and for two months with sodium. Experiment (a) showed a higher vapor pressure in the more recently heated portion, amounting approximately to 0.3 mm. of mercury. The experiment was

TABLE III

SUMMARY OF EXPERIMENTAL WORK

1 Liquid	Acetic acid	Bromine	CCl_4	Benzene (a)	Benzene (b)
2 Time liquid in A had remained at room temp., months	2.5	3	18	22	22
3 Time liquid had been held at the boiling point, hours	4.8	4.0	4.5	4.5	19.1
4 Time required for A to attain temp. equilibrium with bath, minutes	12–18	5	6	5	5
5 Duration of expt. after insertion of A, hours	4.2	3.4	0.5	10.0	0.3
6 Av. press. diff. for first 15 minutes, mm. liquid	−2.5	0.0	−1.0	+4.1	+0.8
7 Av. press. diff. for later observations, mm. liquid	−2.3	+0.1	−1.0	+5.8	+0.5
8 Change of press. diff. between 6 and 7, mm. Hg	+0.014	+0.022	0.000	+0.102	−0.018
9 Change in b. p. indicated by 8 in °C	0.0006	0.0009	0.0000	0.0043	0.0008

continued for ten hours, the difference increasing to 0.4 mm. As it was suspected that the original vapor pressure difference was caused by an impurity, both portions of the benzene were subjected to isothermal distillation. The sample contained in isoteniscope B showed good agreement with the other results for benzene, while that in A showed distinctly greater impurity (probably permanent gas). In order to see if this difference disappeared with equally pure samples, experiment (b) was performed. In this experiment the difference in vapor pressure amounted to only 0.06 mm. of mercury, and isothermal distillation showed almost identical curves for the samples in the two isoteniscopes.

Discussion

The following four points (Table III) are most pertinent to the question of whether the phenomenon reported by Baker has any influence on ebullioscopic determinations.

(1) All liquids had been standing at room temperature for a considerable time before being used, thus assuring attainment of the equilibrium for that temperature.

(2) Except in the case of acetic acid, the isoteniscope which had been plunged into the hot bath gained the temperature of the bath in six minutes or less.

(3) The difference in pressure observed varies in direction, suggesting that it is fortuitous. In benzene (a) the difference was accounted for by an impurity found in one of the isoteniscopes. In acetic acid the difference would amount to only 0.007° difference in boiling point. The striking contrast of this result with Baker's is shown in Table IV.

TABLE IV

COMPARISON OF RESULTS WITH ACETIC ACID

Temp. of obsn., °C.	Pressure difference Mm.	In percentage of satn., press., %	Corresponding temp. diff., °C.	Observer
20	2	17	3	Baker
117.5	0.17	0.002	0.007	Wright

(4) In all cases but benzene (a) there was no perceptible change in the pressure difference produced by continued comparison over a period of time. The case of benzene (a) has been accounted for by a gradual accumulation of permanent gas.

Summary

To determine whether the boiling point of a liquid is altered by prolonged heating at the boiling point, an apparatus was constructed which allows a direct differential vapor pressure measurement to be made upon two samples of a liquid, one sample having been kept at the boiling point for several hours, the other elevated to the boiling point from room tem-

perature immediately before making the observation. Isothermal distillation within the apparatus furnishes a very sensitive test for the purity of the liquid. As the result of observations made on acetic acid, bromine, benzene and carbon tetrachloride, it may be concluded that the vapor pressure of a sample of liquid rapidly elevated to the boiling point is identical with that which it exerts after remaining for several hours at the boiling point. Delay in attaining internal equilibrium is therefore not a factor of influence in the measurement of boiling point or vapor pressure of these liquids, and observations may be made as soon as temperature equilibrium is established.

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